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# PtSi-*n*-Si Schottky-barrier photodetectors with stable spectral responsivity in the 120–250 nm spectral range

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Front-illuminated PtSi-*n*-Si Schottky barrier photodiodes have been developed for the ultraviolet and vacuum ultraviolet spectral range. Their spectral responsivity was determined in the 120–500 nm spectral range by use of a cryogenic electrical substitution radiometer operated with spectrally dispersed synchrotron radiation. For wavelengths below 250 nm, the spectral responsivity is about 0.03 A/W, comparable to that of GaAsP Schottky photodiodes. Unlike the GaAsP diodes, the new PtSi-*n*-Si diodes have a spatially uniform response which is virtually stable after prolonged exposure to short wavelength radiation. Even after a radiant exposure of 150 mJ cm<sup>-2</sup> at wavelength 120 nm, the relative reduction in spectral responsivity remains below 0.2%. Due to these features, this type of photodiode is a promising candidate for use as secondary detector standard in the ultraviolet and vacuum ultraviolet spectral ranges. © 1996 American Institute of Physics. [S0003-6951(96)04250-7]

Among semiconductor photodetectors for the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral ranges, Schottky-barrier photodiodes are appreciated for their outstanding stable performance even under heavy radiant exposure.<sup>1</sup> Therefore, in spite of the fact that silicon *p-n* junction diodes with higher initial quantum efficiency for UV radiation exist,<sup>1</sup> Schottky detectors are considered optimum in those applications, where stability under strong irradiation is a crucial requirement, such as for detector standards or satellite-borne UV astronomy. We report here on a novel PtSi-*n*-Si Schottky photodiode with a spectral responsivity comparable to that of the best GaAsP Schottky detectors but with much higher stability in the vacuum ultraviolet spectral range.

For the development of an irradiation-resistant photodetector, the advantage of Schottky diodes lies in their structure. While in Si *pn* junction diodes, the prolonged exposure to UV or VUV radiation invariably leads to traps in the oxide layer on the photosensitive surface, causing a degradation of the quantum efficiency, this oxide layer is absent in a Schottky barrier diode. The PtSi-Si Schottky contact as photodiode<sup>2</sup> has electrical and chemical features particularly favoring stable performance. It has the second highest barrier on *n*-type Si (up to 0.95 V), a low resistivity of 35  $\mu\Omega$  cm, and very high chemical stability.<sup>3</sup> The favorable features of the PtSi-Si interface originate from the silicide formation process. By depositing Pt onto a chemically clean Si surface and subsequent annealing, the platinum diffuses into the uppermost layers of the substrate, the surface contaminants being thereby diluted in the silicide film or accumulated on the PtSi film surface. The resulting silicide/Si interface is formed in some depth below the original Si surface and can be made atomically clean and therefore metallurgically extremely stable. These features, and the advantages provided by the

use of standard Si technology, have been previously exploited in the fabrication of infrared CCD imagers on the basis of PtSi-*p*-Si photodiodes.<sup>4-6</sup>

The present diodes were fabricated on 25  $\Omega$  cm *n*-type Si(100) wafers by silicon planar technology. The *n*++ contacts and *p*+ guard rings were made by ion implantation, wet etching was employed to remove the protective oxide from the contact areas. The Pt films were deposited by magnetron sputtering in an ordinary high vacuum system (base vacuum of 10<sup>-8</sup> mbar) in Ar plasma, and the silicide was formed by *in situ* after-deposition annealing at 500 °C. The resulting less than 10-nm-thick films were partially epitaxial to the (100) silicon, forming an abrupt, contamination-free, laterally uniform interface between PtSi film and the silicon substrate,<sup>7</sup> as seen in Fig. 1.

Considering the high quality of the interface, shown also by the measured *I*-*V* ideality factors being typically below

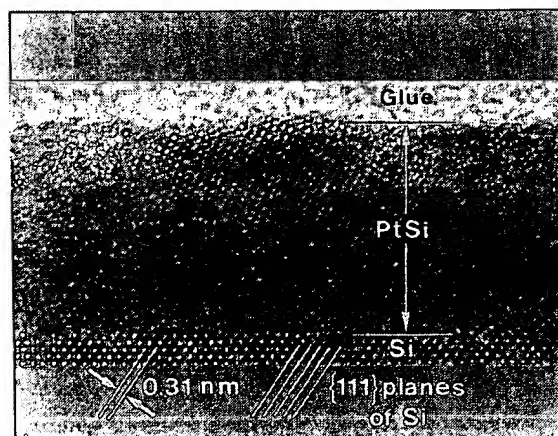


FIG. 1. Micrograph of the transverse section of a 7.5-nm-thick PtSi film on Si(001) (Ref. 7). The film is polycrystalline with isolated grains epitaxial to the substrate, the interface between PtSi film and silicon substrate is abrupt, contamination-free, and laterally uniform.

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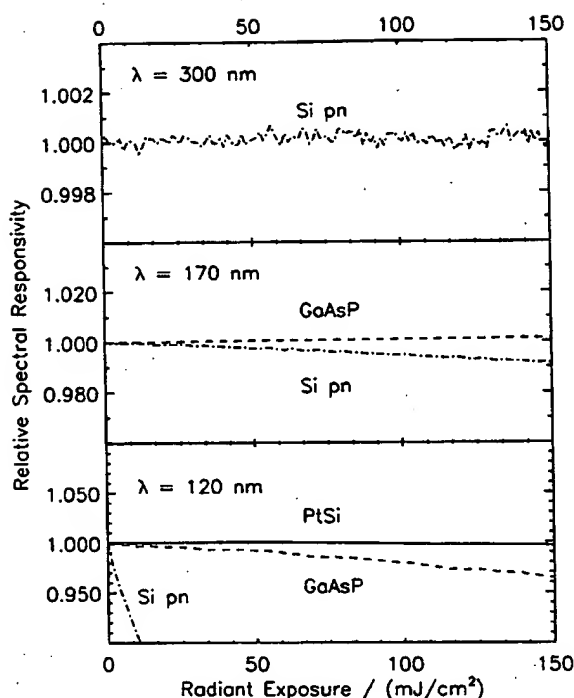


FIG. 2. Relative spectral responsivity vs radiant exposure at different wavelengths for different photodiodes: Si *pn* (Hamamatsu S1337), GaAsP Schottky (Hamamatsu G2119), and PtSi-*n*-Si Schottky (PtSi film thickness 4 nm).

1.02 in the broad temperature range from 100 to 300 K, and the spectral responsivity of the diodes in the visible and near-UV,<sup>7</sup> a reasonably good spectral responsivity was expected in the VUV range. Preliminary measurements at the radiometric calibration facility of the NIST (National Institute of Standards and Technology, Gaithersburg, USA) for wavelengths down to 50 nm confirmed this expectation.<sup>8</sup>

A systematic investigation of the spectral responsivity in the vacuum UV and, in particular, of the stability of the diodes photoresponse under high radiant exposure at different wavelengths, has been undertaken at the VUV radiometry laboratory of PTB (Physikalisch-Technische Bundesanstalt) located at the 800 MeV electron storage ring BESSY in Berlin.<sup>9,10</sup> Particular emphasis was put on measuring stability behavior at wavelengths below 170 nm, in view of the known lack of sufficiently stable semiconductor photodetectors for this spectral range.

The experimental station for detector calibration in the 40–500 nm wavelength range combines a 1 m-15° McPherson-type Rowland-circle normal-incidence monochromator and a cryogenic electrical substitution radiometer.<sup>9,11</sup> Synchrotron radiation of a BESSY 1.5 T bending magnet is focused by a spherical mirror onto the entrance slit of the monochromator, a spherical grating images the radiation in the first spectral order onto the exit slit. An ellipsoidal mirror mounted in grazing incidence focuses the monochromatized synchrotron radiation on the detector. The electrical substitution radiometer and the detector under study can be turned alternately into the beam. Different mirror and grating coatings and various filters are used to suppress radiation from higher spectral orders. A radiant power

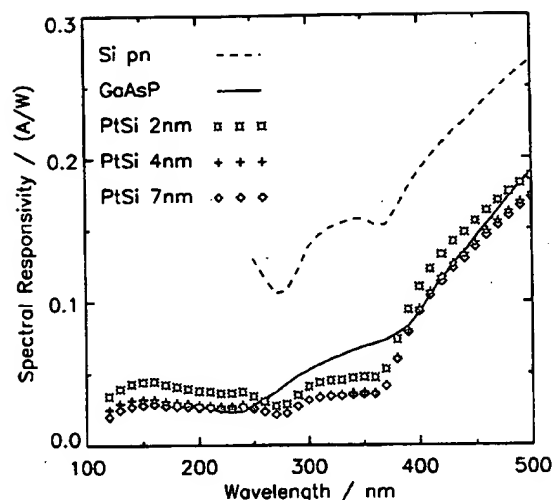


FIG. 3. Spectral responsivity vs wavelength for Si *pn* (Hamamatsu S1337), GaAsP Schottky (Hamamatsu G2119), and PtSi-*n*-Si Schottky photodiodes. For the PtSi diodes, data for three film thicknesses are plotted. The relative uncertainty amounts to  $u=1\%$  for the Si *pn* and the GaAsP photodiode (Ref. 12) and to  $u=3.5\%$  in the case of the PtSi diodes.

of a few  $\mu\text{W}$  is achieved when working at rather moderate resolving power  $\lambda/\Delta\lambda$  of 100. Several photon flux monitor detectors, that cover different spectral ranges, are available to record the monotonic decrease of the photon flux behind the monochromator, while the BESSY beam current slowly decreases with a lifetime of 2–4 h.

The electrical substitution radiometer is used as a primary detector standard for radiant power measurement with a relative uncertainty of well below 1%.<sup>12</sup> It consists of a cavity absorber, thermally linked to a liquid helium cooled reference block but heated to about 1.8 K above the reference block temperature of 4.4 K. The absorber temperature is stabilized and the electrical heater power is measured. Hence, the absorbed radiant power is equal to the difference of the heater power with and without radiation. To minimize uncertainties due to the variation of the thermal background radiation, the last section of the beamline, which includes an aperture system, is cooled to liquid nitrogen temperature, and the vicinity of the cavity to liquid helium temperature.

In order to test the stability of the PtSi diodes, irradiations by synchrotron radiation of different wavelengths were performed. The photocurrent was measured as function of time and divided by the signal of the appropriate photon flux monitor. This ratio, normalized to unity at the first data point, is plotted in Fig. 2 as a function of the radiant exposure, labeled relative spectral responsivity. The radiant exposure  $H$  is calculated from the irradiation time  $t$  and the measured radiant power  $\Phi$  as  $H = A^{-1} \int \Phi dt$ , where  $A$  is the focal area of the beam spot on the detector surface (full width at half maximum), amounting to  $2.9 \text{ mm} \times 1.3 \text{ mm}$  at 100 nm wavelength, for example.

For the sake of comparison, the upper part of Fig. 2 shows the measured time variation of the photoresponse of a commercial Si *pn* photodiode (Hamamatsu S1337), which is used as secondary detector standard in the wavelength range down to 250 nm, under prolonged irradiation at wavelength 300 nm. At this wavelength, for instance, the spectral re-

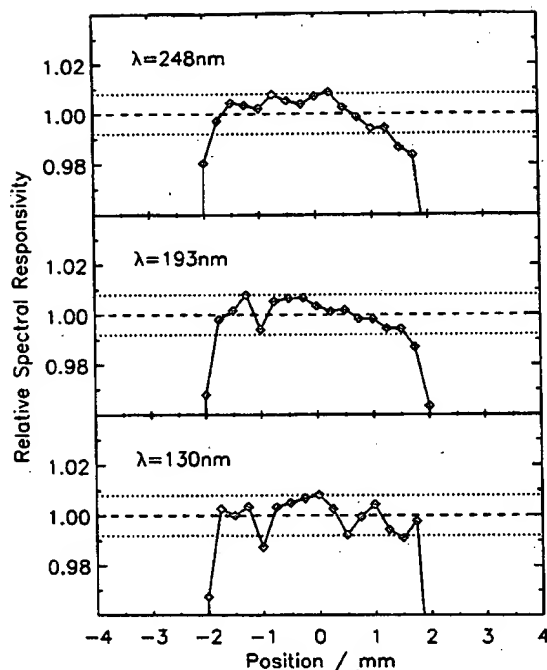


FIG. 4. Relative spectral responsivity across the photoresponsive surface of a PtSi-*n*-Si Schottky diode (PtSi thickness 4 nm) at different wavelengths measured by scanning the photodiode behind a beam defining pinhole of 0.25 mm diam. The dotted lines indicate the estimated detection limit for spatial variations of the spectral responsivity imposed by variation of the photon flux behind the pinhole.

sponsivity of this type of photodiode is stable within few parts in  $10^4$ .<sup>13</sup> Below 250 nm, the Si *pn* diode becomes unstable under irradiation, as is exemplified in Fig. 2 for the wavelengths 170 and 120 nm. The spectral responsivity of commercially available GaAsP Schottky photodiodes (Hamamatsu G2119), on the other hand, is stable for wavelengths down to 170 nm.<sup>13</sup> At wavelength 120 nm, however, even the GaAsP detector is seen to deteriorate fast with increasing radiant exposure, whereas the response of the PtSi-*n*-Si Schottky diode remains practically unchanged.

Clearly, among the two types of Schottky photodiode, the present PtSi-Si diodes are more stable under irradiation in the spectral range below 170 nm, which makes them promising candidates for use as secondary detector standards. In addition, they give a comparable or even higher response than the GaAsP detector for wavelengths below 250 nm. This is shown in Fig. 3 where the spectral responsivity of the same diodes as in Fig. 2 is plotted in the respective spectral domains of stability. PtSi diodes with PtSi film thickness other than 4 nm are included also.

A further aspect for use of a photodiode as detector standard is the homogeneity of the photosensitive surface. The PtSi diodes were therefore scanned in two dimensions across

the synchrotron radiation beam, the spot size of which was confined by a pinhole of 0.25 mm diam. Three central cuts through the resulting responsivity profiles, taken at different wavelengths, are shown in Fig. 4, revealing a remarkable homogeneity: The root mean square (rms) deviation of the measured responsivity across the active diode surface is found to be in the 0.6%–0.8% range, which approximately equals the accuracy of the homogeneity measurement. GaAsP Schottky diodes, on the other hand, show variations of the spectral responsivity of order 10%.<sup>13,14</sup>

In conclusion, the stability of the present silicon-based Schottky photodiodes, having PtSi Schottky contacts of thickness less than 10 nm on *n*-type Si, surpasses that of the best commercially available semiconductor photodetectors in the investigated 120–500 nm spectral region. The high stability of the spectral responsivity is most probably due to the chemically extremely stable silicide-silicon interface and the lack of surface oxide on the photosensitive area. At the same time, the absolute value of their spectral responsivity for wavelengths below 250 nm is roughly the same as that of the best available GaAsP Schottky photodiodes, but with a superior uniformity over the active diode surface of better than the measurement accuracy.

Due to their high stability and homogeneity, the PtSi-*n*-Si Schottky photodiodes are very promising candidates for use as secondary detector standards in the UV and VUV spectral ranges or as photon detectors for satellite-based UV and VUV astronomy. Moreover, the diodes, by their technology, are also suitable for use in front-illuminated UV and VUV sensitive CCD arrays.

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